

Fate of aniline and sulfanilic acid under denitrifying conditions

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A logical concept for the removal of azo dyes in biological wastewater treatment systems is based on anaerobic treatment, for the reductive cleavage of the azo linkages, in combination with aerobic treatment, for the degradation of the products from azo dyes cleavage, aromatic amines (Van der Zee and Villaverde, 2005). A drawback of aerobic treatment is that many aromatic amines from azo dye cleavage are prone to autoxidation, which mostly increases the size of the molecules, thereby reducing their biodegradability. Alternatively, one may consider using nitrate, instead of oxygen, as electron acceptor. Nitrate is a powerful electron acceptor, and it has been reported that at least some aromatic amines can be degraded coupled to nitrate reduction (Kuhn and Suflita, 1989). Moreover, the presence of nitrate does not lead to autoxidation of reduced azo dyes. A further interesting feature of using nitrate is that the first step of denitrification yields nitrite, a compound that has been found to react with aromatic amines, resulting in deamination, thereby yielding aromatics with a higher biodegradation potential than aromatic amines (A.J.M. Stams, personal communication). Although it can be stated that anaerobic-anoxic treatment holds promise as a strategy for azo dye degradation, its potential has never been explored.

With the objective to investigate the fate of aromatic amines under denitrifying conditions, two upflow anoxic bioreactors were operated. The reactors were fed with synthetic wastewaters containing aniline and/or sulfanilic acid (SA) and a mixture of volatile fatty acids (VFA) as the primary electron donors. The terminal electron acceptors were stoichiometric amounts of either nitrate (R1) or a mixture of nitrate and nitrite (R2). Supporting batch denitrification experiments were conducted to monitor toxicity and ultimate biodegradability.

The results demonstrated biodegradation of a substantial fraction of the influent anilineconcentration in R1 (Fig. 1). In contrast, SA was not degraded (data not shown). The presence of nitrite at low pH (influent R2) caused a chemical reaction that led to immediate disappearance of the aromatic amines, resulting in the formation of phenol and two other main compounds (compound 1 and 3). Phenol and compound 1 appeared associated with nitrite-reacted aniline and nitrate-reacted SA, respectively, whereas compound 3 was only formed when both amines were present. Bioreactor treatment removed about half of compound 3, most of the phenol, and mostly all of compound 1, whereas a new metabolite (compound 2) was formed. The overall COD removal was always higher in R1 than in R2, suggesting toxicity of nitrite and/or the products of the chemical reaction between aromatic amines and nitrite.

Whereas a replacement of amino-groups by hydroxyl-groups (as in the observed formation of phenol from aniline) holds promise for biodegradability, the results indicate that the chemical reaction is more complex, resulting in the formation of compounds that were not mineralized during the course of the experiment.

It is the authors' intention to identify compounds 1-3 using LC-MS.

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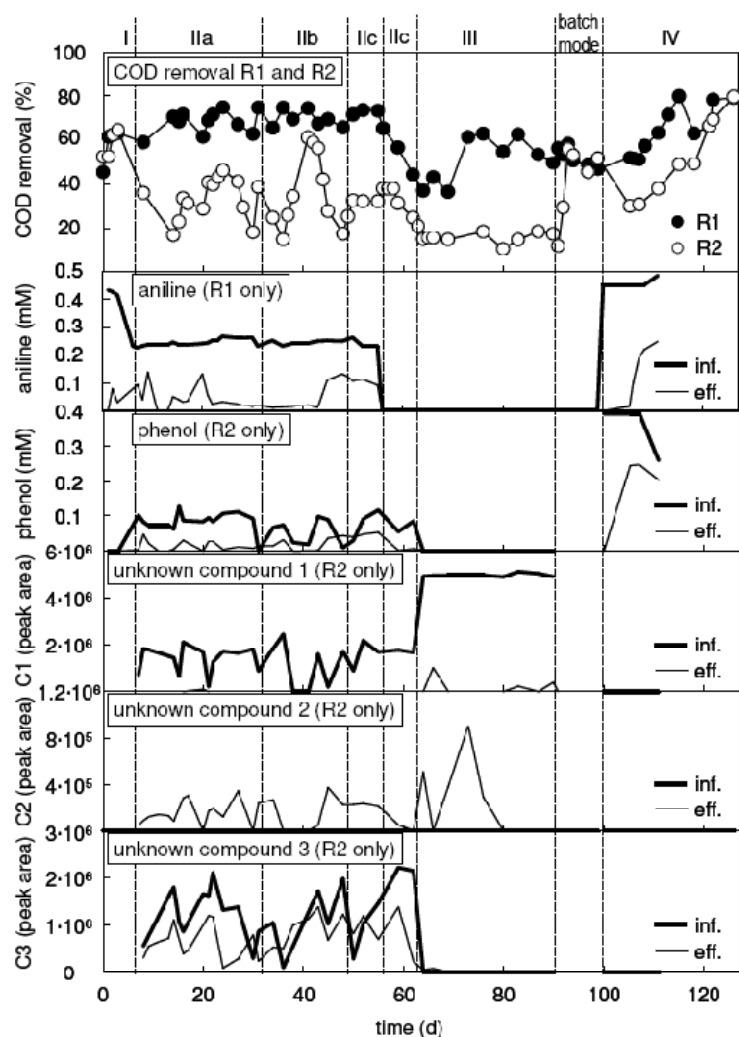


Fig. 1: COD removal and concentrations of aromatic amines and derivatives in influent and effluent of R1 (nitrate) and R2 (nitrate+nitrite). The Roman figures refer to operational phases I: Aniline + SA + 200 mg L⁻¹ VFA-COD, inf.-pH 7; IIabc: Aniline + SA + (a)200, (b)300 and (c)400 mg L⁻¹ VFA-COD, inf.-pH 4.8; III: SA + 300 mg L⁻¹ VFA-COD, inf.-pH 4.8; IV: Aniline + 300 mg L⁻¹ VFA-COD, inf.-pH 4.8.

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